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Communication to the Editor

Photocatalytic Degradation of Lindane in Aqueous Solution*

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Abstract: Photolysis of lindane in aqueous solution, using near-visible and UV light ($\lambda > 320$ nm) and in the presence of the polyoxometallate $PW_{12}O_{40}^{3-}$, results in its conversion to CO_2 and HCl. Initial photodecomposition takes place within a few minutes both in the presence and absence of dioxygen. The effective mineralization in the absence of dioxygen suggests that OH radicals act as the primary oxidant in this case.

Key words: lindane, polyoxometallates, photocatalytic degradation, mineralization

1 INTRODUCTION

Environmental pollution has become a serious problem during the last few decades and it is good that the scientific world has intensified efforts to remedy this problem. Various methods have been used for the decontamination of the aquatic environment. Those that involve electromagnetic radiation consist mainly of treatment with ^{60}Co-γ-radiation, UV light, UV light in the presence of hydrogen peroxide or ozone, and UV and near-visible light in the presence of titanium dioxide, TiO_2.[1]

Recently the photocatalytic mineralization of chlorophenols, i.e., decomposition to CO_2 and HCl, and of a great variety of aromatic and aliphatic pollutants, has been demonstrated using polyoxometallates (POM).[2–4] These are acid condensation products, mainly of molybdenum and tungsten[5,6] that become powerful oxidizing reagents[7] upon excitation with near-visible and UV light, capable of destroying a great variety of pollutants in the aquatic environment.[2–4] Contrary to what was believed so far concerning photoredox processes with POM, the main oxidant seems to be OH radicals generated by reaction of POM with H_2O.[2–4] POM are at least as effective as the widely publicized TiO_2. Dioxygen is important in that it oxidizes (regenerates) the catalyst and through reductive activation may or may not participate further in the process, depending on the substrate.

Lindane (1, 2, 3, 4, 5, 6-hexachlorocyclohexane; predominantly γ isomer) is one of the most seriously persistent pesticides.[8] Although it has been replaced by more polar or photodegradable pesticides, it seems that it will be used for many years to come in the developing countries.

Lindane undergoes hydrolysis under basic conditions, with a half-life of about 50 h at pH 9, but it is totally stable at pH < 5.

Hamada *et al.*[9] reported rapid photodegradation of lindane in 2-propanol by UV light (254 nm) and Prakash *et al.*[10] have reported its photodegradation in methanol in the presence of organic photosensitizers. However, only photodecomposition of lindane is mentioned and no mineralization.

In this paper, we report the complete photodegradation of lindane to CO_2 and HCl in homogeneous aqueous solution by a characteristic

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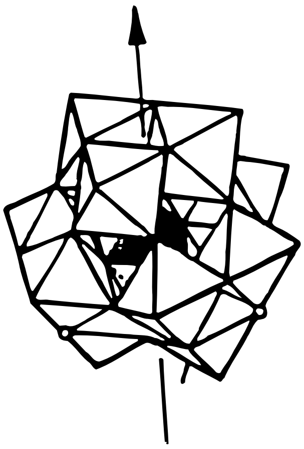

Fig. 1. The structure of $PW_{12}O_{40}^{3-}$ (Keggin structure).[5] The central PO_4 tetrahedron is surrounded by twelve WO_6 octahedra, presenting an overall Td symmetry.

representative of the POM family, $PW_{12}O_{40}^{3-}$ Fig. 1. This compound is stable indefinitely in organic solvents and at pH 1 in aqueous solution.

2 EXPERIMENTAL

2.1 Materials

$PW_{12}O_{40}^{3-}$ was prepared according to methods reported in the literature.[11] Lindane was obtained as solid material from Alltech, Chicago, IL USA, with a purity of 99%. Aqueous solutions containing lindane at 0·037 mM were made by stirring the solid in water for 10 h followed by filtration to remove any undissolved substrate.

The solvents used (dichloromethane and hexane) were pesticide residue-free (Pestiscan; Lab Scan, Dublin Ireland).

2.2 Methods

Aqueous lindane solution (0·037 mM; 4·0 ml) containing catalyst (0·7 mM) was added to a spectrophotometer cell (1 cm long) which was covered with a serum cap. The solution was adjusted to pH 1 using perchloric acid. Photolysis was performed at 20°C, with an Oriel 1000 W Xe arc lamp, equipped with a cool water circulating filter to absorb the near IR radiation and a 320 nm cut off filter to avoid direct photolysis of substrate. The solution was magnetically stirred throughout the experiment. Argon (extra pure) was used for de-aeration and dioxygen for oxygenation.

2.2.1 Analysis of the photolysis solution

The solution (4 ml), was extracted with dichloromethane (3 × 10 ml). The organic layers were combined and transferred through sodium sulfate into a 250-ml round-bottomed flask and the solution evaporated nearly to dryness using a rotary evaporator. Hexane was then added to give a volume of 10 ml. GC-ECD analysis was performed using a Varian Model 3400 gas chromatograph equipped with ECD, split/splitless injection port, a DB-1 fused silica capillary column by J&W Scientific Inc. (30 m × 0·32 mm ID, 0·25 μm film thickness) and autosampler Model 8200 cx; results were evaluated using software from DAPA Scientific Pty Ltd, Kalamunda, Australia.

Chloride ions were analysed spectrophotometrically.[12] Gas samples were analyzed for CO_2 in a VARIAN 3300 gas chromatograph equipped with TCD and a 2-m Porapack Q column. Carbon dioxide content was calculated using a calibration curve, constructed from data obtained with known quantities of CO_2 processed under the same experimental conditions.

The degree of reduction of POM in photolysed deaerated solutions was calculated from the known extinction coefficients of the blue products ($\varepsilon_{750\ nm} = 0{\cdot}2 \times 10^4\ M^{-1}\ cm^{-1}$),[11] using a Perkin Elmer Lambda 19 spectrophotometer.

3 RESULTS AND DISCUSSION

Photolysis of an aqueous solution of lindane in presence of $PW_{12}O_{40}^{3-}$ at $\lambda > 320$ nm to avoid direct photolysis of substrate, resulted in its eventual complete photodegradation, i.e. formation of CO_2 and HCl. This process takes place in the presence and absence of dioxygen but no photodegradation of lindane takes place in the absence of catalyst under these conditions.

In the absence of dioxygen, no regeneration (reoxidation) of catalyst takes place, at least in the first stages of photolysis. Thus, the accumulation of the blue colour of the one-electron reduced tungstate, $PW_{12}O_{40}^{4-}$, with photolysis time, could be followed (Fig. 2). Photoreduction of $PW_{12}O_{40}^{3-}$ results in concomitant oxidation of lindane.

Figure 3 shows the photodegradation of lindane, the formation of the reduced catalyst ($PW_{12}O_{40}^{4-}$) and the accumulation of CO_2 and Cl^- with photolysis time. The induction period involved prior to evolution of CO_2 is indicative of intermediates involved. The photoreduced tungstate greatly exceeded the stoichiometry of lindane from the first few minutes of photolysis (Fig. 3). However, the concentration of lindane was reduced to zero after 2–3 h of photolysis (Fig. 3). It appears, then, that the intermediates involved react competitively with the catalyst from the initial stages of photoreaction. However, despite the slow initial generation of Cl^- and CO_2, complete mineralization of lindane occurred after 5 to 10 h of photolysis. (Data not shown.)

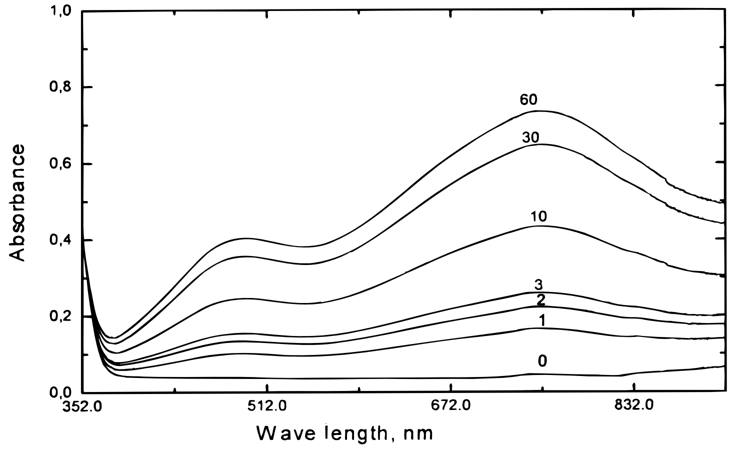

Fig. 2. Gradual formation of the one-electron reduced POM, $PW_{12}O_{40}^{4-}$, suggesting concomitant oxidation of lindane, upon photolysis ($\lambda > 320$ nm) of de-aerated aqueous solution of lindane (0·037 mM) in presence of $PW_{12}O_{40}^{3-}$ (0·7 mM). Photolysis time (min) is indicated on spectra.

POM are known to react as redox catalysts in the following general way:

$$POM + S \rightarrow POM_{red} + S_{ox} \quad (1)$$

$$POM_{RED} + \text{oxidant} \rightarrow POM + \text{oxidant products} \quad (2)$$

where S = substrate.

Excitation of $PW_{12}O_{40}^{3-}$ at the $O \rightarrow M$ CT bands ($\lambda < 400$ nm) enhances its oxidative ability by ≈ 3 eV.[7,13] Thus, various top priority pollutants undergo mineralization in presence of $PW_{12}O_{40}^{3-}$ in aqueous solution,[2–4] including lindane.

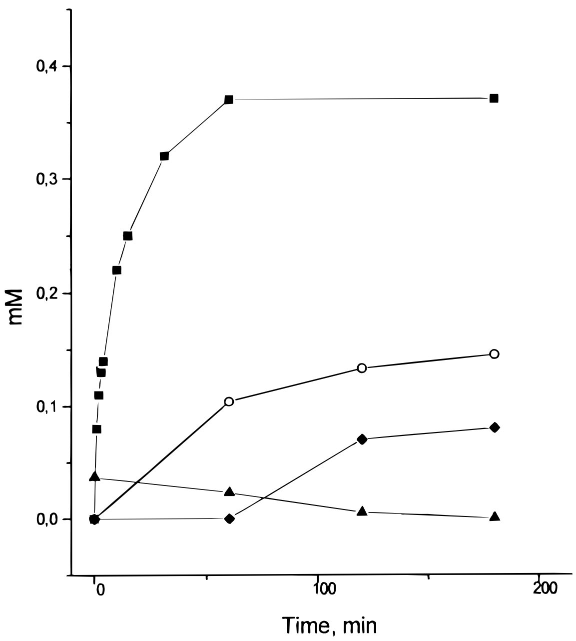

Fig. 3. Photodegradation of lindane and formation of one-electron reduced catalyst, $PW_{12}O_{40}^{4-}$, CO_2 and Cl^-, upon photolysis of an aqueous deoxygenated solution of lindane in the presence of $PW_{12}O_{40}^{3-}$. Solution volume 4 ml; $PW_{12}O_{40}^{3-}$ (0·7 mM); lindane (0·037 mM); pH, 1 ($HClO_4$); $\lambda > 320$ nm; T, 20°C. (■) $PW_{12}O_{40}^{4-}$; (○) CL^-; (▲) lindane; (◆) CO_2.

The characteristic photochemical reactions that take place, as have been suggested by the results of this and prior work[2–4,7] are as follows:

$$PW_{12}O_{40}^{3-} \xleftrightarrow{h\nu} [PW_{12}O_{40}^{3-}]^* \quad (3)$$

$$[PW_{12}O_{40}^{3-}]^* + H_2O \longleftrightarrow PW_{12}O_{40}^{4-} + OH + H^+ \quad (4)$$

$$PW_{12}O_{40}^{4-} + O_2 \longleftrightarrow PW_{12}O_{40}^{3-} + O_2^- \quad (5)$$

$$OH + \text{lindane} \rightarrow \text{oxidation products} \quad (6)$$

$$O_2^- + \text{lindane} \rightarrow \text{oxidation products} \quad (7)$$

OH radicals should be a primary oxidant in the photodecomposition of lindane, (reactions 4 and 6) for mineralization of lindane is effective, also, in the absence of dioxygen.

The mineralization reaction may be presented as follows:

$$C_6H_6Cl_6 + 15/2\ O_2 \xrightarrow{h\nu,\ POM} 6\ CO_2 + 3\ H_2O + 6\ Cl^- \quad (8)$$

where POM = $PW_{12}O_{40}^{3-}$.

The intermediates involved in the process, as well as the use of other POM to optimize the mineralization of lindane are under investigation.

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REFERENCES

1. Legrini, O., Oliveros, E. & Brown, A. M., Photochemical processes for water treatment. *Chem. Rev.*, **93**, (1993) 671–98.

2. Mylonas, A. & Papaconstantinou, E., Photocatalytic degradation of chlorophenols to CO_2 and HCl with polyoxotungstates in aqueous solution. *J. Mol. Catal.*, **92**, (1994) 261–7.
3. Mylonas, A. & Papaconstantinou, E., On the mechanism of photocatalytic degradation of chlorinated phenols to CO_2 and HCl by polyoxometalates. *J. Photochem. Photobiol. A: Chem.*, **94**, (1996) 77–82.
4. Mylonas, A., Roussis, V. & Papaconstantinou, E., Photocatalytic degradation of phenol and *p*-cresol by polyoxotungstates. Mechanistic implications. *Polyhedron*, **15**, (1996) 3211–17.
5. Pope, M. T., Heteropoly and isopoly oxometalates. In *Inorganic Chemistry Concepts* **8**, ed. C. K. Jorgensen *et al.* Springer Verlag, West Berlin, 1983.
6. Day, V. W. & Klemperer, W. G., Metal oxide chemistry in solution: The early transition metal polyoxoanions. *Science* (*Washington*), **228**, (1985) 533–41.
7. Papaconstantinou, E., Photochemistry of polyoxometallates of molybdenum and tungsten and/or vanadium. *Chem. Soc. Rev.*, **18**, (1989) 1–31.
8. Lindane, EHC 124, IPCS, WHO, Geneva 1991, p. 37 and references therein.
9. Hamada, M., Kawano, E., Kawuamura, S. & Shiro, M., Radiation- and photo-induced degradation of five isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane. *Agric. Biol. Chem.*, **45**, (1981) 659–65.
10. Prakash, S., Tandon, G. S., Seth, T. D. & Joshi, P. C., The role of reactive oxygen species in the degradation of lindane and DDT. *Biochem. Biophys. Res. Commun.*, **199**, (1994) 1284–8.
11. Pope, M. T. & Varga, G. M. Jr, Heteropoly blues. I. Reduction stoichiometries and reduction potentials of some 12-tungstates. *Inorg. Chem.*, **5**, (1966) 1249–54.
12. Florence, T. M., Spectrophotometric determination of chloride at the parts-per-billion level by the mercury (II) thiocyanate method. *Anal. Chim. Acta*, **54**, (1971) 373–7.
13. Papaconstantinou, E., Ioannidis, A., Hiskia, A., Argitis, P., Dimoticali, D. & Korres, S., Photocatalytic processes by polyoxometalates. Splitting of water. The role of dioxygen. In *Polyoxometalates*: *From Platonic Solids to Anti-retroviral Activity*, ed. M. T. Pope & A. Muller. Kluwer, Dordrecht, 1993, pp. 327–35.